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(54) Single-stage hydrotreating process.

(57) A process for catalytically hydrotreating hydrocarbon oils having a tendency to deactivate hydrotreating catalysts by coke formation, in the presence of hydrogen at elevated temperature and pressure which comprises passing:

a) oils having a final boiling point greater than 538 °C and containing less than 2%w of heptane asphaltenes,

b) oils having a final boiling point from 343 °C–538 °C, or

c) mixtures thereof,

downwardly with a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to H_2S; wherein said stacked-bed comprises an upper zone containing 15–85%v, basis total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal, metal oxide or metal sulphide and a phosphorus compound and a lower zone containing 15–85%v, basis total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal, metal oxide or metal sulphide, and less than 0.5%w phosphorus and separating the reacting product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having reduced sulphur and/or heavy metal content.

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SINGLE-STAGE HYDROTREATING PROCESS

The present invention relates to a single-stage hydrorefining process for treating heavy oils using catalysts arranged in a particular manner, referenced to herein as "stacked bed". It particularly relates to a single-stage hydrorefining process for treating oils having a tendency to deactivate hydrotreating catalysts by coke formation, these being oils with high boiling components and/or oils with a low asphaltene content and very high boiling components, with a particular stacked bed catalyst arrangement. It has been found that the use of a stacked bed increases the catalyst life or allows increased conversions relative to the more traditional catalysts used for the treating of these oils. The invention is particularly useful for meeting the demands of increasing hydrotreatment severity, such as sulphur removal, for poorer quality heavy oil fractions both directly distilled or extracted from crude or crude fraction and oil fractions from thermal, steam, or catalytic cracking processes including mixtures of any of these materials.

The continual changes in the refining industry such as the trend to poorer quality crudes and the continual increase in the stringency of oil product specifications (e.g. lower allowed sulphur content) is in part requiring the refiner to increase the severity of hydrotreating of traditional oil fractions and/or process fractions not traditionally treated. The increased severity and/or unusual feed generally have been causing increased deactivation of hydrotreating catalysts. By using the process according to the present invention the run length of a hydrotreating process with these oil fractions can be increased and/or higher severity operation and/or processing poorer quality oils can be allowed.

The use of lower price or locally available crudes frequently results in increased sulphur and/or nitrogen content of the oil fractions. Conversion processes such as thermal cracking, coking

and catalytic cracking are either being brought on-stream or are already processing poorer quality oils. The products from such processes are laden with heteroatoms such as sulphur and are more hydrogen deficient relative to products from better quality crudes or oils distilled directly from crude or crude fractions. As a result, the products of the conversion processes and/or poorer crudes have to be additionally hydrotreated to meet specifications or to prepare for further treating/conversion. However, the higher operating temperatures required to remove the additional heteroatoms and adding additional hydrogen in addition to the hydrogen-deficient coke-like nature of these feeds result in increasing deactivation of the hydrotreating catalysts due to coking. Any increase in hydrotreating catalyst activity and/or stability would enable refiners to upgrade the lower value poor quality and/or cracked oils at a significant economic benefit.

It is well known that hydrogen-deficient poor quality oils can be hydrotreated/hydrorefined with low catalyst deactivation rates at higher hydrorefining unit conditions - higher hydrogen pressure, and/or hydrogen-to-oil ratio, and/or oil-catalyst contact time. To stay within the physical or design constraints of a unit or to continue to process the required volumes of oil, only relatively small variations in these parameters can be made. As a result, very expensive hydrotreating equipment must be added to meet the changing goals unless catalysts with longer lives are available. Alternatively, the refiner has to accept very short catalyst lives and increased down time for frequent catalyst changes or use continuous or semicontinuous regeneration facilities. Larger and/or more vessels and additional equipment would be needed to process a given quantity of feedstock with these options. Of particular importance to a refiner is the ability to process the hydrogen-deficient and/or poorer quality oils in existing hydrotreating units which do not have sufficient hydrogen pressure to prevent uneconomically rapid catalyst activity loss with existing catalysts utilized in a non-stacked bed configuration. Thus, improved processes and highly stable catalysts are in great demand.

Several two-stage hydrotreating processes have been proposed in the art to overcome some of the difficulties of hydrotreating heavy oils. Reference is made to five patent specifications, wherein use is made of two catalyst reactor vessels.

In U.S. patent specification 3,766,058 a two-stage process is disclosed for hydrodesulphurizing high-sulphur vacuum residues. In the first stage some of the sulphur is removed and some hydrogenation of the feed occurs, preferably over a cobalt-molybdenum catalyst supported on a composite of ZnO and Al_2O_3. In the second stage the effluent is treated under conditions to provide hydrocracking and desulphurization of asphaltenes and large resin molecules contained in the feed, preferably over molybdenum supported on alumina or silica, wherein the second catalyst has a greater average pore diameter than the first catalyst.

In U.S. patent specification 4,016,049 a two-stage process is disclosed for hydrodesulphurizing metal- and sulphur-containing asphaltenic heavy oils with an interstage flashing step and with partial feed oil bypass around the first stage.

In U.S. patent specification 4,048,060 a two-stage hydrodesulphurization and hydrodemetallization process is disclosed wherein a different catalyst is utilized in each stage and wherein the second stage catalyst has a larger pore size than the first catalyst and a specific pore size distribution.

In U.S. patent specification 4,166,026 a two-step process is taught wherein a heavy hydrocarbon oil containing large amounts of asphaltenes and heavy metals is hydrodemetallized and selectively cracked in the first step over a catalyst which contains one or more catalytic metals supported on a carrier composed mainly of magnesium silicate. The effluent from the first step, with or without separation of hydrogen-rich gas, is contacted with hydrogen in the presence of a catalyst containing one or more catalytic metals supported on a carrier, preferably alumina or silica-alumina, having a particular pore volume and pore size distribution. This two-step method is claimed to be more efficient than a conventional

process wherein a residual oil is directly hydrodesulphurized in a one-step treatment.

In U.S. patent specification 4,392,945 a two-stage hydrorefining process for treating heavy oils containing certain types of organic sulphur compounds is disclosed wherein use is made of a specific sequence of catalysts with interstage removal of H_2S and NH_3. A nickel-containing conventional hydrorefining catalyst is present in the first stage. A cobalt-containing conventional hydrorefining catalyst is present in the second stage. The first stage is preferably operated under conditions to effect at least 50 %w desulphurization, while the second stage is preferably operated under conditions to achieve at least about 90 %w desulphurization, relative to sulphur present in the initial oil feed to the first stage. This process is primarily applicable to distillate gas oil feeds boiling below 343 °C which contain little or no heavy metals.

All of the patent specifications referred to hereinabove relate to two-stage hydrotreating processes for various hydrocarbon oils utilizing certain advantageous catalysts and/or supports. In some of these processes removal of H_2S and NH_3 is required. However, no reference is made in any of the afore-mentioned patent specifications to a process whereby oils with final boiling points from 343 °C to 538 °C and/or oil with a low asphaltene content and with components boiling above 538 °C can be hydrotreated with significantly improved catalyst life relative to a single catalyst system. It has now been found that by using a specific stacked-bed catalyst arrangement containing different catalytically active compositions, oils with high boiling components (about 343 °C - 538 °C and/or oils with a low asphaltene content and with very high boiling components (above 538 °C) can be treated in a single stage hydrotreating process with improved catalyst-system life and/or increased hydrotreating conversions for a given feedstock. The process according to the present invention allows easy conversion of existing catalytic hydrotreating reactors to a stacked bed of specified catalysts. The present process operates well at hydrogen

pressures below 75 bar (7500 kPa), so that no additional high pressure reactors need be constructed. The particular stacked bed combination of catalysts in accordance with the invention results in longer runs between replacements or regenerations for a given oil than would be experienced with either catalyst used alone. Alternatively, poorer quality oils can be processed at equivalent conversions or higher conversions for a given oil can be maintained with the same time between replacement or regeneration with the use of the single-stage stacked bed catalyst system according to the present invention. The invention can be applied most usefully in situations where rapid catalyst deactivation is occurring.

The present invention thus relates to a process for catalytically hydrotreating hydrocarbon oils at elevated temperature and pressure in the presence of hydrogen by passing:

a) oils having a final boiling point greater than 538 °C and containing less than 2 %w of heptane asphaltenes,

b) oils having a final boiling point from 343 °C to 538 °C, or

c) mixtures thereof,

downwardly with hydrogen or a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to hydrogen sulphide; wherein said stacked-bed comprises an upper zone containing 15-85 %v, basis total catalyst, of a hydrotreating catalyst comprising a component from Group VIB of the Periodic Table, a Group VIII metal, metal oxide or metal sulphide and a phosphorus oxide and/or sulphide, and a lower zone containing 15-85 %v, basis total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal, metal oxide or metal sulphide and less than 0.5 %w of phosphorus; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having a reduced heteroatom content.

The process according to the present invention is particularly suitable for systems where catalyst deactivation due to coking is a constraint. The bottom bed catalyst is preferably Ni-promoted when

nitrogen removal is the predominant concern and is preferably Co-promoted when sulphur removal is the predominant concern.

According to the present invention oils having a) final boiling points above 538 °C whilst having a heptane asphaltenes content less than about 2% by weight, b) final boiling points in the range between 343 °C and 538 °C, or c) mixtures thereof are contacted with hydrogen or a hydrogen-containing gas and passed downwardly under hydrodesulphurization conditions over a stacked-bed catalyst. The boiling points referred to in the present description are as defined by the American Society for Testing And Materials (ASTM) method D 2887-83 ("Boiling Range Distribution of Petroleum Fractions by Gas Chromatography") and is commonly known as TBP-GLC (true boiling point by gas liquid chromatography). Normal heptane asphaltenes (asphaltenes) as discussed herein are measured by the Institute of Petroleum, London, method IP 143/78 ("Asphaltenes Precipitation with Normal Heptane").

The oils to be used as feedstock in the process according to the present invention will be oils having a tendency to deactivate hydrotreating catalysts by coke formation, under hydrotreating conditions and particularly under hydrodesulphurization conditions.

Downwardly has been used in this specification to indicate a direction and not an orientation and hence should not be construed to imply an orientation limitation on the instant invention. A downwardly series flow of oil and gas through a reactor is the usual pattern; however, one could invert the reactor conceptually and put oil and gas in at the bottom in which the first catalyst zone (Ni- and P-containing catalyst) should be the first main catalyst contacted by the oil and gas and would thus be in the bottom of the first reactor. As is well known in the industry, multiple reactors connected in series are placed individually. Oil and gas out of one reactor is piped up to the top of the next reactor; however, this process could be inverted. The above-described reactor configurations, as well as others apparent to those skilled in the art, are deemed to be within the scope of this invention.

The feedstocks to be applied in the process in accordance with this invention may be taken from straight run oils (non-cracked) or thermally-, steam-, or catalytically cracked hydrocarbonaceous materials. Suitable feeds include petroleum derived gas oils distilled from crude or crude fractions at atmospheric or at reduced pressure; solvent extracted oils such as extracted oils commonly referred to as Deasphalted Oils; thermally or steamed cracked oils or fractions thereof such as coker gas oils; gas oils or cycle oils from catalytic cracking and mixtures of two or more of the above materials.

Multiple uses of these feedstocks after initial treating in accordance with the process according to the present invention are also possible. Depending on particular feedstocks treated, suitable uses may include feed and additions to feed to units for significant molecular weight reduction such as catalytic cracking units or hydrocracking units; direct use or by blending with other oils or additives for sale as transportation fuels such as diesel oils; or for refinery fuel.

The stacked-bed catalyst system to be used in the process according to the present invention comprises firstly a normally Ni- and P-containing conventional hydrotreating catalyst. The second catalyst to be contacted by the oil normally comprises a low- or no-phosphorus content conventional catalyst. Preferably, the second catalyst contains no phosphorus. The second catalyst is also a conventional catalyst and contains Ni and/or Co in the formulation. When desulphurization is the primary objective of the hydrotreating process, the second catalyst contains Co in preference to Ni; when denitrogenation is the primary objective, the second catalyst preferably contains Ni in preference to Co. The catalysts herein can be prepared by techniques well known in the art. The advantages of this invention primarily accrue from the particular combination of operable hydrotreating catalysts in a stacked-bed rather than from any particular method or manner of fabricating the catalyst.

The first main hydrotreating zone catalyst used in the process according to the present invention suitably comprises a Ni- and

P-containing conventional hydrotreating catalyst. Conventional hydrotreating catalysts which are suitable for the first catalyst zone generally comprise a phosphorus oxide and/or sulphide component and a component, selected from group VIB of the Periodic Table and a group VIII metal, metal oxide, or metal sulphide and/or mixtures thereof composited with a support. These catalysts will contain up to 10 %w, usually 1 to about 5 %w of the group VIII metal compound calculated basis the metal content, from 3 to about 15 %w of the group VIB metal compound calculated basis the metal content, and from 0.1 to 10 %w phosphorus compounds calculated basis phosphorus content. Preferably, the catalyst comprises a nickel component and a molybdenum and/or tungsten component with an alumina support which may additionally contain silica. A more preferred catalyst comprises a nickel component, a molybdenum component, and a phosphorus component with an alumina support which may also contain small amounts of silica. Preferred amounts of components range from 2 to 4 %w of a nickel component calculated basis metal content, 8-15 %w of a molybdenum component calculated basis metal content, and 1 to 4 %w, more preferably 2 to 4 %w, of a phosphorus component calculated basis the phosphorus content. The catalyst can be used in any of a variety of shapes such as spheres and extrudates. The preferred shape is a trilobal extrudate. Preferably, the catalyst is sulphided prior to use, as is well known to the art.

The use of low-phosphorus or no-phosphorus catalysts in the second zone is thought to be of benefit due to reduced deactivation by coking.

Low-phosphorus content catalysts having high surface areas (greater than about 200 m^2/g) and high compacted bulk densities (0.6-0.85 g/cm^3) are preferably used for the second zone as they appear to be highly active. The high surface area increases reaction rates due to generally increased dispersion of the active components. Higher density catalysts allow one to load a larger amount of active metals and promoter per reactor volume, a factor which is commercially important. The metal content specified above

provides high activity per reactor volume. Lower metal contents normally result in catalysts exerting too low activities for proper use in the process according to the present invention. Higher metal loadings than specified above do not contribute significantly to the performance and thus lead to an inefficient use of the metals resulting in high catalyst cost with little advantage. Since deposits of coke are thought to cause the majority of the catalyst deactivation, fresh catalyst pore volume should be at or above a modest level (0.4-0.8 cm^3/g, more narrowly 0.5-0.7 cm^3/g). The second zone catalyst can be used like the first zone catalyst in a variety of shapes. Preferably, the catalyst is sulphided prior to use as is well known to the art.

The Ni-containing catalyst used for the first zone is preferably a high activity conventional catalyst suitable for high levels of hydrogenation. Such catalysts have high surface areas (greater than 140 m^2/g) and high compacted bulk densities (0.65-0.95 g/cm^3, more narrowly 0.7-0.95 g/cm^3). The high surface area increases reaction rates due to generally increased dispersion of the active components. Higher density catalysts allow one to load a larger amount of active metals and promoter per reactor volume, a factor which is commercially important. The metal and phosphorus content specified above provides the high activity per reactor volume. Lower metal contents result in catalysts exerting too low activities for proper use in the process according to the present invention. Higher metal contents do not contribute significantly to the performance and thus lead to an inefficient use of the metals and higher cost for the catalyst. Since deposits of coke are thought to cause the majority of the catalyst deactivation, fresh catalyst pore volume should be at a modest level (0.4-0.8 cm^3/g, more narrowly 0.4-0.6 cm^3/g).

A low-phosphorus or no-phosphorus conventional hydrotreating catalyst is used in the second zone of the catalyst system. Co and/or Ni containing conventional catalysts can be suitably applied. The second zone catalyst differs from the first zone catalyst primarily in its low-phosphorus content (less than 0.5 %w). The

preferred catalyst contains less than about 0.5 %w phosphorus and comprises a component from group VIB and a group VIII metal, metal oxide, or metal sulphide and/or mixtures thereof composited with a support. Preferably, the catalyst comprises a nickel and/or cobalt component and a molybdenum and/or tungsten component with an alumina support which may additionally contain silica. Preferred metal contents are up to 10 %w, usually 1 to 5 %w of group VIII metal component(s) calculated basis the metal content, and from 3 to 30 %w of group VIB metal component(s) basis the metal content. A more preferred catalyst comprises a cobalt or nickel component and a molybdenum component with an alumina support.

The present invention preferably relates to a process for hydrotreating oils having a tendency to deactivate hydrotreating catalysts by coke formation, by passing a) oils having a final boiling point above 538 °C and having less than 2 %w of heptane asphaltenes, b) oils having a final boiling point from 343 °C to 538 °C, or c) mixtures thereof downwardly with hydrogen or a hydrogen-containing gas (mixture) into a hydrotreating zone over a stacked-bed of two hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to H_2S, wherein said stacked-bed comprises an upper zone containing of from 15-85 %v, basis total catalyst, of a high-activity hydrotreating catalyst which comprises from 2-4 %w nickel, from 8-15 %w molybdenum and from 1-4 %w phosphorus supported on a carrier consisting mostly of alumina, and a lower zone containing of from 15-85 %v, basis total catalyst, of a high-activity, hydrodesulphurization catalyst which comprises from 2-4 %w cobalt and/or nickel, from 8-15 %w molybdenum and less than 0.5 %w phosphorus supported on a carrier consisting mostly of alumina; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid oil having reduced sulphur and/or heavy metal content.

The physical characterizations of the catalysts referred to herein are common to those skilled in the catalyst development art. Surface areas refer to nitrogen adsorption surface areas preferably determined by at least three points. Pore size distributions are

determined by mercury intrusion and calculated with a 130 degree contact angle. Pore volumes stated are water pore volumes and indicate the volume of water per weight of catalyst necessary to fill the catalyst pores to an incipient wetness of the catalyst.

The volume of the first catalyst zone in the present invention is from 15 to 85 %v of the main catalyst charge. The remaining fraction of the main catalyst charge is composed of the second catalyst. The division of the catalyst volumes over the zones in the bed depends upon the requirement for nitrogen conversion versus the requirements for stability and other hydrotreating reactions such as sulphur and metals removal. Stacked-beds can be used to tailor the amount of nitrogen removal, sulphur and metals removal, and system stability. An increase in the first catalyst will increase the nitrogen removal but will effect the hydrodesulphurization (HDS) activity and stability of the system. Below a catalyst ratio of 15:85 or above a catalyst ratio of 85:15 (upper:lower) the benefits for the stacked-bed system are not large enough to be of practical significance. There is no physical limit on using a smaller percentage of one or the other beds.

The catalyst zones referred to herein may be in the same or different reactors. For existing units with one reactor the catalysts are layered one on top of the other. Many hydrotreating reactors consist of two or more reactors in series. The catalyst zones are not restricted to the particular volume of one vessel and can extend into the next (prior) vessel. The zones discussed herein refer to the main catalyst bed. Small layers of catalysts which are different sizes are frequently used in reactor loading as is known to those skilled in the art. Intervessel heat exchange and/or hydrogen addition may also be used in the process according to the present invention.

The pore size of the catalyst does not play a critical role in the process according to the present invention. The catalysts in the two zones may be based upon the same carrier. Normally, the finished catalysts will have small differences in their average

pore sizes due to the differences in the respective metal and phosphorus loadings.

Suitable conditions for operating the catalyst system in accordance with the present invention are given in Table I.

TABLE I

Conditions	Broadest range	Broad range	Narrow range	Narrowest range
Hydrogen partial pressure, bar	6.8-75	20-75	20-55	34-55
Total pressure, bar	13.6-95	27-95	27-75	47-75
Hydrogen/feed ratio, Nl/kg feed	17-1780	17-890	51-255	85-255
Temperature, °C	150-455	285-455	285-425	345-425
Liquid hourly space velocity, kg/kg.h	0.1-10.0	-	0.5-5.0	-

At temperatures below 285 °C (for very heavy feeds) and below 150 °C (for heavy feeds), the catalysts do not exhibit sufficient activity for the rates of conversion to be of practical significance. At temperatures above 455 °C the rate of coking and cracking become excessive resulting in increasingly impractical operations. Reactor metallurgy may also be a limitating constraint above 455 °C at the higher pressures.

At liquid space velocities below 0.1 kg/kg.h, the residence time of the oil is long enough to lead to thermal degradation and coking. At liquid space velocities above 10 kg/kg.h the conversion across the reactor is too small to be of practical use. For space

velocity and gas-to-oil ratio calculations referred to herein, volumes are measured at 15.5 °C and atmospheric pressure.

Hydrogen partial pressure is very important in determining the rate of catalyst coking and deactivation. At pressures below 6.8 bar, the catalyst system cokes too rapidly even with better quality oil containing high boiling components. At pressures above 75 bar, the deactivation mechanism of the catalyst system appears to be predominantly that of metals deposition, if present, which results in pore-mouth plugging. Catalysts of varying porosity can be used to address deactivation by metals deposition, as is known by those skilled in the art. The hydrogen to feed ratio to be applied in the process according to the present invention is required to be above 17 Nl/kg feed since the reactions occurring during hydrotreating consume hydrogen, resulting in a deficiency of hydrogen at the bottom of the reactor. This deficiency may cause rapid coking of the catalyst and leads to impractical operation. At hydrogen to feed ratios in excess of 890 Nl/kg feed, no substantial benefit is obtained; thus the expense of compression beyond this rate is not warranted.

Nitrogen removal is an important factor in hydrotreating heavy oils. Catalysts without phosphorus can be more stable with heavy oils under the conditions noted above; however, nitrogen removal activity is low for no-phosphorus catalysts relative to their phosphorus promoted counterparts. Additionally, Co promoted catalysts are less active for nitrogen removal than are Ni promoted catalysts. Stacked catalyst beds can be used to tailor the amount of nitrogen removal, sulphur and metals removal, and system stability. It has been found that a stacked-bed system also improves activities (other than nitrogen removal) as well as the stability of the overall catalyst system relative to either catalyst used individually. The stacked-bed catalyst system is applicable when processing feeds under conditions where a heavy feed is causing deactivation primarily by coking.

The process according to the present invention should be operated at conditions suitable to remove at least 25% and gene-

rally conditions will be applied to remove 30-80%, more preferably 45-75%, of the sulphur in the feed. When metals such as Ni and V are present in the feed and demetallization is the primary focus the process can be operated at the lower levels of desulphurization. When there is little metal in the feed and demetallization is not the primary goal, one can operate the process at higher sulphur removal rates.

The invention is accompanied by Figures 1 and 2 wherein some of the results as described in the Examples are depicted graphically.

Figure 1 represents a graph showing the advantage obtained in the reactor inlet temperature as a function of time when the stacked-bed according to the present invention is utilized.

Figure 2 represents a graph showing the advantage obtained in the reactor outlet temperature as a function of time when the stacked-bed according to the present invention is utilized.

The following Examples are presented to illustrate the present invention.

EXAMPLE 1

A catalyst A containing nickel, molybdenum and phosphorus supported on a gamma alumina carrier was prepared from commercially available alumina powders. This carrier was extruded into 1.6 mm pellets having a trilobal cross section. The pellets were dried and calcined before being impregnated with the appropriate catalytically active metals by a dry pore volume method i.e., by adding only enough solution to fill the alumina pore volume. Carriers containing in addition to alumina, a few per cent of other components like silica or magnesia can also be applied. An appropriate aqueous solution of nickel nitrate, nickel carbonate, phosphoric acid, hydrogen peroxide, and ammonium molybdate was used to impregnate the carrier. The metal loadings and some properties of the dried, calcined catalyst (A) are given in Table II.

A catalyst B containing cobalt and molybdenum supported on a similar alumina carrier as used to prepare catalyst A was prepared. Likewise, this carrier was also extruded into 1.6 mm pellets having

a trilobal cross-section. The pellets were dried before being impregnated with the appropriate catalytically active metals by a dry pore volume method. An appropriate aqueous solution of cobalt carbonate, ammonium dimolybdate and ammonia was used to impregnate the carrier. The metal loadings and properties of the dried, calcined catalyst (B) are also given in Table II.

TABLE II

Catalyst	A	B
Diameter	1.6 mm	1.6 mm
Cross-section	Trilobal	Trilobal
Composition, %w		
Ni	3.0	-
Co	-	3.2
Mo	13.0	9.6
P	3.2	-
Compacted bulk density, g/cm^3	0.82	0.71
Surface Area, m^2/g	164	226
Hg-pore volume, cm^3/g	0.47	0.61

Three different commercial runs with a main catalyst charge of a Ni-Mo-P/alumina catalyst, a Co-Mo/alumina catalyst and a stacked-bed of a Ni-Mo-P/alumina catalyst over a Co-Mo/alumina catalyst were carried out. In Fig. 1 the reactor inlet temperature (RIT in °C) necessary to maintain 0.3% weight sulphur in the product is graphically represented as a function of time (days), which is a convenient measure of general catalyst activity. The Ni-Mo-P catalyst data are represented as circles (upper line), the Co-Mo catalyst data as triangles (middle line) and the stacked catalyst data as diamonds (lower line). The stacked-bed system has good activity and stability for sulphur removal as well as denitrification advantages. The average feed properties and average unit

conditions are given in Table III. The feed applied was a heavy vacuum gas oil having a final boiling point above 538 °C and containing less than 2 %w of heptane asphaltenes. Feed to the unit and unit conditions were remarkably constant during the runs considering the unit is a commercial unit. In the stacked-bed system the Ni-Mo-P catalyst formed about 33% of the main catalyst load while the Co-Mo catalyst made up the remainder of the main catalyst load. Oil and gas flowed in a single-stage and serially over first the Ni-Mo-P catalyst and then over the Co-Mo catalyst.

The main advantages of the stacked-bed system shown by this Example comprise a) a significant increase in catalyst stability as can be seen in Fig. 1 where the increase in RIT with time is significantly less for the stacked-bed system (3.1 °C/month versus 12.5 °C/month) relative to the single catalyst system; b) an increase in catalyst activity as represented by about a 8.1 °C lower initial RIT for the same level of sulphur in the product; c) a resulting greatly improved estimated catalyst life of about 400% for the stacked-bed relative to the single bed due to the improvements in activity and stability. An end of run temperature of 416 °C and a continued linear decline rate was used to estimate the catalyst life of the stacked-bed system.

TABLE III

Feed/Process properties	
Hydrogen partial pressure 38 bar	
Liquid hourly space velocity	3 kg/kg.h
Sulphur, % wt	1.1
Nickel, ppm	0.6
Vanadium, ppm	0.7
RCR, % wt	0.3
TBP-GLC, °C	
IBP/10%	265/347
90/95%	524/538

EXAMPLE 2

A second set of two commercial runs with a Ni-Mo-P/alumina catalyst and a stacked-bed of a Ni-Mo-P/alumina catalyst over a Co-Mo/alumina catalyst was also carried out. A Ni-Mo-P/alumina catalyst would be one that one skilled in the art would traditionally have chosen for this feedstock when considering hydrogenation, denitrification, and desulphurization catalyst activity rather than a Co-Mo catalyst. Table IV summarizes approximate average unit conditions and feedstock. The oil is a blend of straight run vacuum gas oil (distilled from non-cracked oil) and a coker heavy gas oil. In Table V the approximate average performance for the two runs at two catalyst ages is summarized and in Figure 2 the reactor outlet temperature necessary to maintain 0.75% weight and 0.60% weight sulphur in the product for the single catalyst and the stacked bed system is depicted as a function of time (days).

The main advantages of the stacked-bed system relative to the single bed system shown by this Example comprise a) higher sulphur conversion, even at lower operating temperatures, b) greater catalyst stability when processing the same type feed — about

first 60 days --, c) processing a heavier feed at comparable stabilities -- about after 60 days --, and d) greater hydrogen addition even at lower operating temperatures. It can be seen from Fig. 2 that the single bed system has a lower start of run temperature in the first one or two weeks but this temperature relates to 0.75 %w sulphur in the product where the temperature for the stacked-bed system relates to 0.60 %w sulphur in the product. To obtain also 0.6 %weight sulphur in the product initially with the single bed system an additional 7.5 °C would be required, thereby making the single bed about 4.4 °C less active initially. It will be clear from Fig. 2 that although the two different catalyst configurations have similar temperatures at the start of run (for the different sulphur targets), the stacked-bed system has about a 12.5 °C advantage after 2 months indicating the greater stability when processing the same type feed containing about 30% by volume of the coker material. After about 60 days the coking tendency of the feed to the single bed system was reduced by decreasing the amount of the full range coker heavy gas oil from about 30% down to 20% by volume (indicated by an arrow in the upper line of Fig. 2). The single bed system stability improved with the feed having reduced coking tendency and is beginning to approach that of the stacked-bed system although still at the higher sulphur in product level. This data shows that the stacked-bed system can be used to process a feed with greater coking tendency with equivalent catalysts life and for this case even with higher sulphur conversion. Table V provides some data indicating that the hydrogen consumption of the stacked-bed system is some 6% better (lower) than that of the single bed system. The best comparison is at the 1 month point where the catalysts are processing the same feed. The larger hydrogen consumption is reflected in the greater temperature rise across the reactor (Reactor delta T in Table V); hydrogen addition is a major factor in the heat release during hydrotreating.

TABLE IV

Feed properties and operating parameters		
Feed	Vacuum gas oil/ coker heavy gas oil	
Ratio	40/60	
End Point, °C	above 538 °C	
Feed Sulphur, %w	~3	
LHSV, kg/kg.h	2.76	
H_2 pressure (Reactor inlet) bar	49.3	
H_2/oil ratio (Nl/kg feed)	289	
Individual feedstocks	**Vac. gas oil**	**Coker heavy gas oil**
Molecular weight	369	312
Carbon, %w	85.4	85.2
Hydrogen, %w	11.8	11.0
Sulphur, %w	2.5	3.2
TBP-GLC wt		
538 °C	91.2	95.0

TABLE V

Catalysts and performance				
Catalyst age	1 month		4 months	
Catalyst*	1	1 & 2	1	1 & 2
Reactor temp., out, °C	360	357.2	376.7	362.8
Reactor delta T, °C	37.5	40.6	34.4	40.6
H_2 consumption, Nl/kg feed	63.8	68	63.8	68
Product sulphur, %w	0.75	0.6	0.75	0.6

* Catalyst 1 is Ni-Mo-P
Catalyst 2 is Co-Mo

EXAMPLE 3

A third set of two commercial runs with a Ni-Mo-P/alumina catalyst and a stacked-bed of a Ni-Mo-P/alumina catalyst and a Co-Mo/alumina catalyst was also made. The feed used has a final boiling point between 343 °C and 538 °C and contained straight run light gas oil, coker naphtha, coker light gas oil and light cycle oil. In Table VI the approximate average unit conditions and feed stock properties are summarized. Analysis of the data for these two runs showed that the stacked-bed used in accordance with the present instant invention showed the following advantages when compared to the single catalyst:

a) lower inlet temperature,

b) lower sulphur in the product, and

c) the ability to operate at the same reactor delta temperature even though the reactor inlet temperature was lower.

TABLE VI

Feed properties and operating parameter

Feed gravity	0.92
Distillation, °C, end point	455
Feed sulphur, %w	1.3
Liquid hourly space velocity kg/kg.h	2.6
H_2 pressure (reactor inlet, bar)	35.4
H_2/oil ratio, Nl/kg feed	168.3

C L A I M S

1. A process for catalytically hydrotreating hydrocarbon oils at elevated temperature and pressure in the presence of hydrogen, which comprises passing:

a) oils having a final boiling point greater than 538 °C and containing less than 2 %w of heptane asphaltenes,

b) oils having a final boiling point from 343 °C to 538 °C, or

c) mixtures thereof,

downwardly with hydrogen or a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to hydrogen sulphide, wherein said stacked-bed comprises an upper zone containing 15-85 %v, basis total catalyst, of a hydrotreating catalyst comprising a component from Group VIB of the Periodic Table, a Group VIII metal, metal oxide or metal sulphide and a phosphorus oxide and/or sulphide, and a lower zone containing 15-85 %v, basis total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal, metal oxide or metal sulphide and less than 0.5 %w of phosphorus; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having a reduced heteroatom content.

2. A process according to claim 1, wherein a stacked-bed is used containing an upper zone containing up to 10 %w of a Group VIII component, 3-15 %w of a Group VIB component and 0.1-10 %w of phosphorus, and a lower zone containing up to 10 %w of a Group VIII component and 3-30 %w of a Group VIB component.

3. A process according to claim 1 or 2, wherein a stacked-bed is used containing an upper zone comprising a nickel component, a molybdenum and/or tungsten component and phosphorus on an alumina support which may additionally contain silica, and a lower zone

comprising a nickel and/or cobalt component and a molybdenum and/or tungsten component on an alumina support which may additionally contain silica.

4. A process according to claim 3, wherein a stacked-bed is used containing an upper zone containing 2-4 %w of nickel, 8-15 %w of molybdenum and 1-4 %w of phosphorus supported on a carrier consisting mostly of alumina, and a lower zone containing 2-4 %w of cobalt and/or nickel, from 8-15 %w of molybdenum and less than 0.5 %w of phosphorus supported on a carrier consisting mostly of alumina.

5. A process according to any of claims 1-4, wherein a stacked-bed is used wherein the upper zone catalyst has a compacted bulk density of 0.65-0.95 g/cm^3, in particular 0.76-0.88 g/cm^3 and a surface area greater than 140 m^2/g, in particular greater than 150 m^2/g, and wherein the lower zone catalyst has a compacted bulk density of 0.6-0.8 g/cm^3, in particular 0.67-0.69 g/cm^3 and a surface area greater than 180 m^2/g, in particular greater than 200 m^2/g.

6. A process according to any one of claims 1-5, wherein the process is carried out at a hydrogen pressure not exceeding 75 bar.

7. A process according to any one of claims 1-6, wherein use is made of a stacked-bed catalyst containing in its lower zone 2-4 %w of cobalt and essentially no nickel and no phosphorus.

8. A process according to any one of claims 1-6, wherein use is made of a stacked-bed catalyst containing in its lower zone 2-4 %w of nickel and essentially no cobalt and no phosphorus.

9. A process according to any one of claims 1-8, wherein use is made of a stacked-bed containing a trilobally shaped catalyst in the upper and/or the lower zone.

10. A process according to claim 9, wherein use is made of a catalyst carrier extruded into a trilobal shape before impregnation.

11. A process according to any one of claims 1-10, wherein the hydrotreating zone is contained in a single reactor and the upper

zone of the stacked-bed catalyst comprises about one-third of the total catalyst volume.

12. A process according to any one of claims 1-11, wherein hydrocarbon oils having a tendency to deactivate hydrotreating catalysts by coke formation are hydrotreated by passing:

a) oils having a final boiling point above 538 °C and having less than 2 %w of heptane asphaltenes,

b) oils having a final boiling point from 343 °C to 538 °C, or

c) mixtures thereof,

downwardly with hydrogen or a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of two hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to H_2S; said stacked-bed comprising an upper zone containing of from 15-85 %v, basis total catalyst, of a high-activity hydrotreating catalyst which comprises from 2-4 %w nickel, from 8-15 %w molybdenum and from 1-4 %w phosphorus supported on a carrier consisting mostly of alumina, said catalyst having a compacted bulk density of 0.65-0.95 g/cm^3 and a surface area greater than 140 m^2/g; and a lower zone containing from 15-85 %v, basis total catalyst, of a high-activity, hydrodesulphurization catalyst which comprises from 2-4 %w cobalt and/or nickel and from 8-15 %w molybdenum and less than 0.5 %w phosphorus supported on a carrier consisting mostly of alumina, said catalyst having a compacted bulk density of 0.6-0.8 g/cm^3 and a surface area greater than 180 m^2/g; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having reduced sulphur and/or heavy metal content.

13. A process according to any one of the preceding claims, substantially as described hereinbefore, with particular reference to the Examples.

14. Hydrotreated hydrocarbon oils whenever obtained by a process according to one or more of claims 1-13.

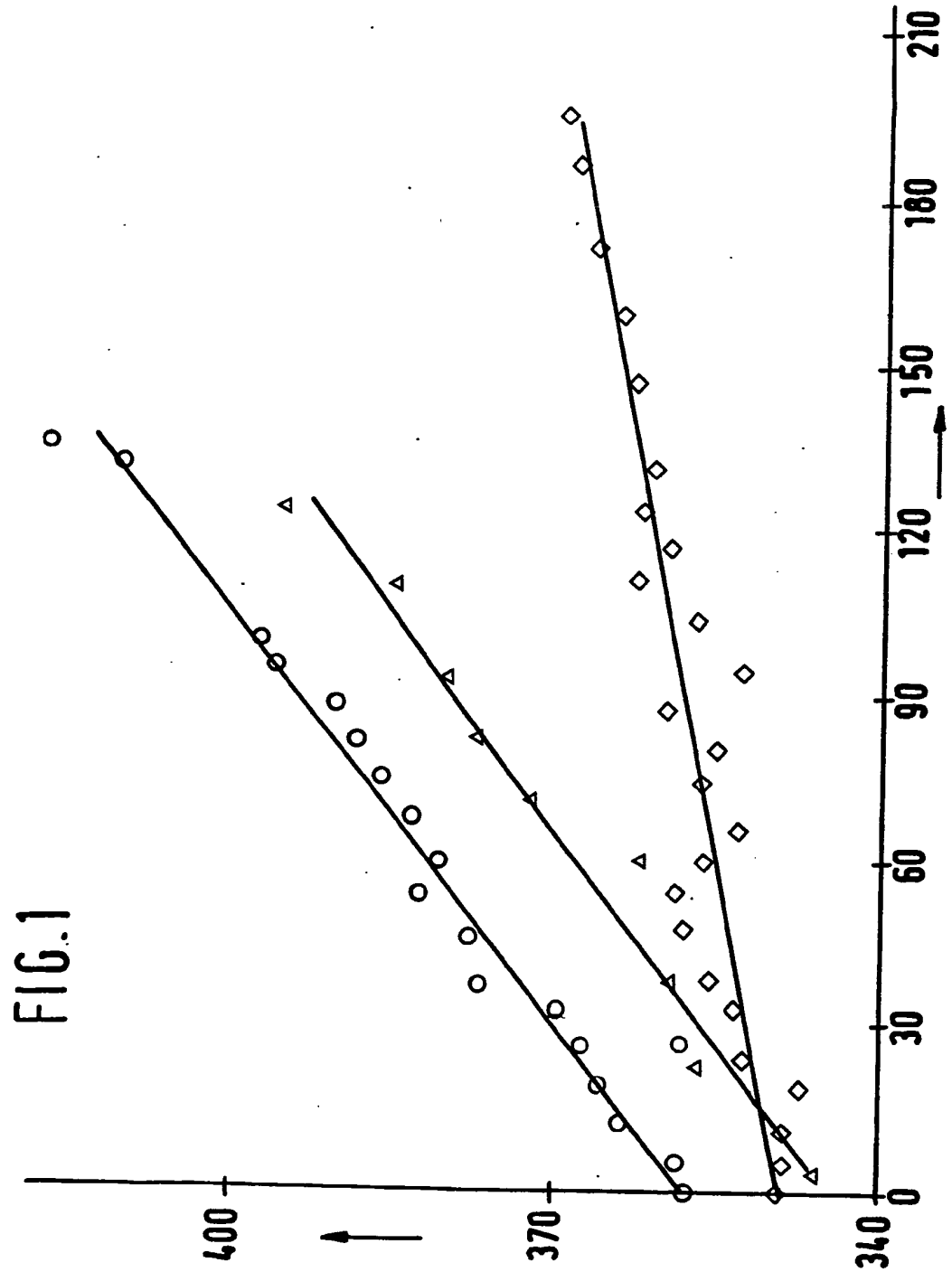
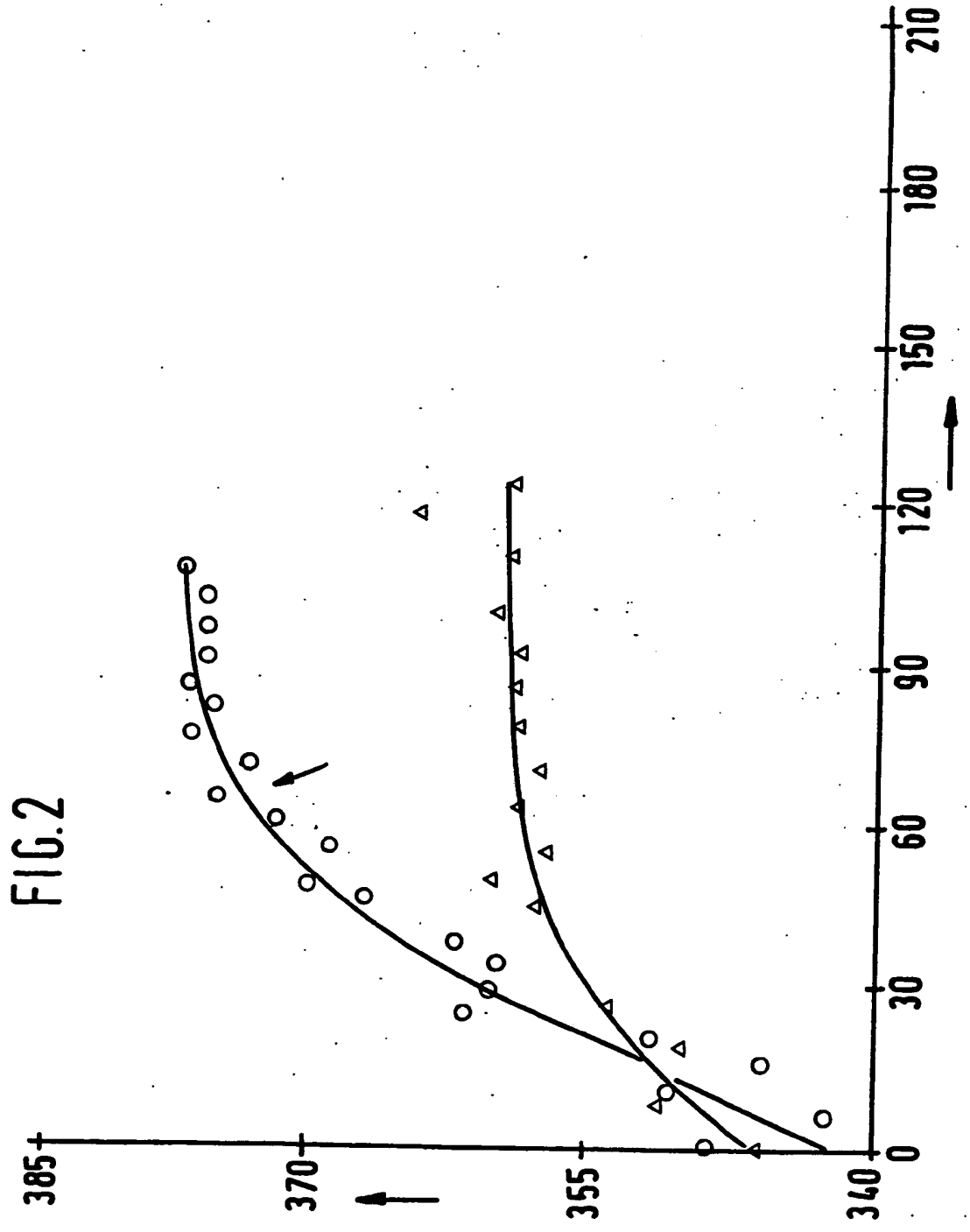


FIG.1

FIG.2



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EUROPEAN SEARCH REPORT

Application number

EP 85 20 1248

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	GB-A-2 032 796 (STANDARD OIL) * Claims 1-15; column 5, lines 72-80 *	1-14	C 10 G 65/04
Y	US-A-4 016 067 (FISCHER et al.) * Claims 1-3 *	1-14	
Y	EP-A-0 126 250 (UNION OIL COMP. OF CALIFORNIA) * Claims 1-28 *	2-5,12	
Y	EP-A-0 112 667 (STANDARD OIL) * Claims 1-17 *	2-5,12	
Y	EP-A-0 008 424 (BASF) * Claims 1,2 *	9,10	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
Y	US-A-4 406 779 (HENSLEY et al.) * Claims 1,4-6,10,11 *	1-14	C 10 G
A	FR-A-2 212 417 (BASF) * Claims 1,2 *		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-08-1986	MICHIELS P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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